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APPLICATIONS OF THE MICROSCAN 9 MICROANALYSER. (U)

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SUMMARY

The basic principles of electron microprobe analysis are outlined, and the essential features of the Microscan 9 instrument described. Applications of the M9 are illustrated by means of practical examples.

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## 1 INTRODUCTION

The M9 is a computer-controlled electron probe microanalyser which is used to obtain information on the chemical composition of small regions, typically down to about 1 $\mu$ m diameter. The purpose of this Memorandum is to outline the principles of operation of the instrument and to indicate its functions and capabilities with some typical examples of its applications.

## 2 BASIC PRINCIPLES

A sufficiently energetic beam of electrons (the electron probe) incident on a specimen will generate X-rays which have energies and wavelengths characteristic of the individual elements of which the specimen is composed. These X-rays are analysed to yield information on the elements present in the specimen. There are two methods of detecting and counting the X-rays; these are known as energy dispersive and wavelength dispersive systems.

In the energy dispersive system, X-rays pass through a protective beryllium window into a solid state detector of silicon treated with lithium and held at liquid nitrogen temperature. The X-rays interact with the silicon and produce voltage pulses, the amplitudes of which are proportional to the X-ray energy. The pulses are amplified and fed into a multichannel analyser which separates pulses of different amplitude into several hundred channels and allows them to accumulate. Thus a spectrum is built up, and when the multichannel analyser is calibrated, peaks corresponding to the elements present in the specimen are obtained. Essentially, a rapid, qualitative or semi-quantitative simultaneous analysis of all the elements in the specimen (except those with atomic number  $Z < 11$ ) may be performed, and a visual presentation of the entire spectrum is available when data accumulation is initiated.

In the wavelength dispersive system, crystals are used to diffract X-rays of a particular wavelength into counters (ie when Bragg's Law is obeyed). Thus only X-rays from the element under consideration are analysed at any one time. The counter is a gas-filled proportional type which produces pulses whose voltage is proportional to the energy of the X-rays, and so an X-ray count rate (counts per second) is obtained for a particular element in the specimen.

In quantitative work, the X-ray count rates for elements in the specimen are compared to those from standards of known composition (often pure elements), while maintaining constant operating conditions. To a first approximation, the ratio of count rates for the specimen to that for the standard gives the concentration of the element in the specimen. However, in practice, differences between the specimen and standard influence X-ray generation and corrections have to be made. Much effort has gone into creating methods for making the corrections, and these are known as ZAF correction procedures since they allow for atomic number (Z), absorption (A) and fluorescence (F) effects.

## 3 DESCRIPTION OF THE M9 SYSTEM

The M9 is a computer-controlled instrument with an energy dispersive detector and two fully focussing spectrometers each containing three crystals. The fact that the

spectrometers are fully focussing means that for all Bragg angles covered ( $15-66^\circ$ ), the X-ray source, the crystal surface and the X-ray counter all lie on the same circle (Rowland circle). Each spectrometer has two counters in tandem; one xenon gas sealed counter for heavy elements, and in front of that either an ordinary flow counter (Channel A) or a light element flow counter (Channel B). The flow counters use argon - 10% methane gas. All elements with  $Z \geq 11$  can be detected with the energy dispersive system, while the spectrometers cover all elements from boron ( $Z = 5$ ) to uranium ( $Z = 92$ ).

The specimen stage, spectrometers and X-ray counters are controlled with commands given to the computer via the teletype, with manual operation by a 'tracker ball' for stage and spectrometer movements when necessary. Electron imaging functions (including image processing) are basically as for a normal scanning electron microscope with area scans, line scans and spot mode possible. The accelerating voltage can be varied from 1-60 kV, with probe currents from about  $10^{-9}$  up to  $5 \times 10^{-6}$  A possible. Polaroid and 35mm cameras are available for image recording, and an X-Y plotter is used to record energy dispersive X-ray spectra. In addition, X-ray peaks from the spectrometers can be acquired using a chart recorder.

There is a binocular microscope for preliminary surveys and setting up, as well as a monocular microscope for viewing the specimen while analysis is in progress. A Faraday cage can be inserted into the electron beam, and the probe current set to the required level by monitoring it on a digital meter. This meter is also used to monitor specimen current, magnification and accelerating voltage.

The computer is also used to perform other operating functions, eg move the stage to specimen change position, insert or withdraw the Faraday cage. Additionally, data collection and processing is handled by the computer, and results printed out on the teletype. An important feature is the ZAF program which enables corrected quantitative data to be acquired. All the necessary data for the ZAF corrections is held in the computer memory, in the 'standards tables', which also contain information for measurements on standards and unknowns, eg stage co-ordinates of standard, spectrometer channel and crystal, Bragg angle, counter variables, standard count rate, kV, probe current. Approximate data in the tables is updated each time the standards are measured, ie Bragg angle, probe current, kV, standard count rate, and then referred to during measurements on the unknown.

Stage and spectrometer repeatability are  $\pm 2 \mu\text{m}$  and  $\pm 0.00167^\circ$ , respectively, with the absolute Bragg angle accurate to  $\pm 0.042^\circ$ . Quoted values for limit of detectability are 0.001% for Cu and 0.01% for C at an absorbed current of 0.1  $\mu\text{A}$ . Absolute accuracy for quantitative analysis is a function of specimen, standard quality, operating conditions and efficiency of the ZAF correction procedure. Normally totals for an analysis should be  $100\% \pm 1$  or  $2\%$ .

The specimen is usually mounted using conventional metallographic techniques, and the surface should be clean, flat and polished. It is placed in a specimen holder, with the standards block, and is situated normal to the electron beam in the instrument. Non-

conducting specimens need to be made conducting, eg by carbon coating. Qualitative work is possible on fracture surfaces.

#### 4 APPLICATIONS

There are basically two types of work which can be carried out; (a) qualitative or semi-quantitative and (b) fully quantitative analysis. Examples of applications will be given for these two types in turn.

##### 4.1 Qualitative and semi-quantitative analysis

Initially it is often desired to ascertain or confirm the elements present in the specimen. An area of interest is first selected using the optical microscope or TV mode electron image at low magnification. The specimen position is set by focussing the optical image using the Z-axis control, and the kV and probe current set as required.

Electron images of a high strength Al-Zn-Mg-Cu alloy containing inclusion stringers, formed using backscattered electrons and the absorbed specimen current are shown in Fig 1a&b respectively. Backscattered electrons are usually used, although the absorbed current image is sometimes useful for showing extra detail. Additional image processing (gamma control, grey levels etc) are also possible. Initial element identification is best done using the energy dispersive system.

##### 4.1.1 Energy dispersive analysis

The spectra, obtained on the X-Y plotter, for spot analyses from the matrix and two types of inclusion are shown in Figs 2 to 4. The analysis points are indicated by A, B and C in Fig 1. Peaks corresponding to Al, Cu and Zn are readily seen in Fig 2, and that of Mg is partly overlapped by the Al peak. (The argon peak is anomalous, possibly originating from the gas of the proportional counters.) The spectra were obtained under identical operating conditions and hence differences in peak heights indicate the relative amounts of each element for each spot analysed, ie spot B is rich in Fe and Cu, and spot C rich in Mg and Si. Thus semi-quantitative information on the chemical composition of the inclusions has been obtained. It is of course also possible to obtain spectra for area and line scans, as well as for the spot analyses.

##### 4.1.2 X-ray images

X-ray images are produced by using the computer to set the appropriate spectrometer to accept the characteristic X-rays of interest, and displaying each pulse as a bright spot on the visual display, which is scanned in synchronisation with the electron probe. Thus the image consists of a large number of spots, the brighter areas indicating a higher concentration of the element in that area. The energy dispersive system can also be used, but generally gives poorer images.

Examples are given in Fig 1c-f, corresponding to the area shown in the electron image above. The inclusion stringers clearly contain two types of inclusion, one rich in Cu and Fe, the other rich in Mg and Si. Mg and Cu also exist in solid solution or in fine precipitates, as indicated by background levels.

At low magnifications, using the crystals, defocussing will occur resulting in a loss of intensity at the edges of the image, ie the electron probe deviation is so large that Bragg's Law is not precisely obeyed. 'Hybrid' scanning, in which the electron probe is scanned in the Y-axis only and the specimen stage is automatically stepped in the X-axis, may be used at magnifications of 150X and 300X to overcome this.

#### 4.1.3 Line scans

Line scans are graphs of the concentration variation for a particular element against distance along a line on the specimen surface. They are obtained by a slow, single scan across the specimen with a spectrometer set up for the element of interest. The deflection of the spot moving across is proportional to the count rate.

An example, corresponding to the line X-X in Fig 1a, is given in Fig 5. Once again the coincidence of Cu and Fe, and of Mg and Si, is apparent. Line scans give a better indication of relative concentration than X-ray images, and are useful for investigating segregation, composition of closely spaced particles etc.

#### 4.1.4 Step scanning of specimen

The computer can be used to step the specimen stage in the X or Y directions (or at a specified angle or in a raster) at set increments over a set distance. At each point, the count rate for the elements specified is printed out on the teletype, as illustrated in Fig 6. In this example the specimen was stepped in the X-direction in 0.03mm steps for 0.24 mm, the probe current being  $5 \times 10^{-8}$  A. At each point the X, Y and Z co-ordinates are printed out, and the element, spectrometer channel and angle, and the count rate (counts per second) are also given, in this case f.r Mg only. In the example, the count rate rises from about 450 c/s to about 4500 c/s and down again, ie the scan passes through an Mg-rich inclusion.

A graphical representation may be obtained using the chart recorder, with the rate-meter output being fed to the recorder input. The example of Fig 7 shows plots for Cu and Mg, peaks occurring where the probe impinges on Cu- and Mg-rich inclusions. The specimen current is also monitored, and appears to be decreased somewhat when the probe impinges on inclusions, particularly the Cu-rich ones.

Step scanning gives similar data to slow line scans, but is useful for programmed raster scans, and scans over large distances, when defocussing would affect slow line scans.

#### 4.1.5 Spectral scanning

This mode of operation is used to scan the spectrometers in conjunction with the chart recorder to obtain a graphical record of a peak. The spectrometer is stepped through a certain angle at set increments and the count rates recorded on the chart recorder, which is also stepped as required. An example is shown in Fig 8, which was obtained by setting the electron probe on a Cu-rich particle and stepping the spectrometer from  $22-23^\circ$  in  $0.005^\circ$  steps using the appropriate crystal. With the energy dispersive system available, spectral scanning is not often necessary to determine the



elements present, but it could be useful for graphical records of peaks for light elements, or for observing the shape of peaks.

#### 4.2 Fully quantitative analysis

For fully quantitative work a clean, flat, polished specimen surface is required, and all measurements on both standards and specimen should be made under the same operating conditions. The general analysis program (GAP) used for quantitative work includes warnings to the operator of deviations in kV or probe current, although small variations in probe current are acceptable and corrected for automatically. The standards are first measured, using the parameters stored in the standards table. An example is given in Fig 9. The general analysis program is entered, specifying the operating kV (GAP; 25). The elements selected in this case were Al, Zn, Mg, Cu, Zr, Fe and Si (MPS;), with the average of three analyses being taken for each element (AVS; 3). The probe current was  $5 \times 10^{-8}$  A. On the command GO the program automatically sets up the stage and spectrometers for each element in turn, performs a peak search to optimise the Bragg angle, obtains count rates and averages these if more than one analysis is specified, and updates the standard tables with the kV and probe current used, standard count rate, Bragg angle and ZAF correction factor.

The results are listed in columns, which from the left give (Fig 9); element, spectrometer channel and peak angle, peak c/s, positive background c/s, negative background c/s, peak minus background c/s, standard deviation ( $2\sigma$ ) c/s, and standard ZAF factor.

Having measured the standards, the points or areas of interest in the unknown specimen are analysed. An example, from a spot analysis in the matrix in Fig 1a, is given in Fig 10. Still in the GAP mode, the command UNK is used to set up either a single point analysis (as in the present case) or a series of points along a line or in a raster, ie the stage can be stepped in the X and/or Y axes and an analysis performed at each point. The elements to be included are specified (STD;) and if a ZAF correction is required this is also typed in. The command GO initiates the program.

The results format for the uncorrected data is similar to that for the standards measurements, but the last two columns are uncorrected concentration (%) and standard deviation ( $2\sigma$ ) of the uncorrected concentration. When ZAF has been specified, the three columns printed out are uncorrected concentration (%), corrected concentration (%) and corrected compound concentration. The centre column, corrected concentration, is generally of most interest. When more than one analysis is specified, an average of all the points is also given at the end.

Compound standards are used for elements such as nitrogen, oxygen, sulphur, and the standard tables are easily modified to allow for the use of such standards. An alloy of known composition could be used as a compound standard for analyses of similar alloy types, as long as the standard is homogeneous on a microscopic scale. The advantage of using such a standard is that a small ZAF correction is required and an immediate comparison of the unknown and standard without ZAF correction is possible.

5 CONCLUDING REMARKS

It is clear that the M9 is a powerful tool for the acquisition of data on the chemical composition of small areas. Computer control has greatly speeded up a potentially laborious technique. The instrument is useful for any application where variations in chemical composition on a microscale need to be evaluated, eg segregation, diffusion of particular elements, identification of inclusions, contamination by undesirable substances etc. Results may be presented in a variety of ways, depending on the particular requirement, and a range of work from qualitative analysis of fracture surfaces to fully quantitative analysis of carefully prepared microsections is possible.

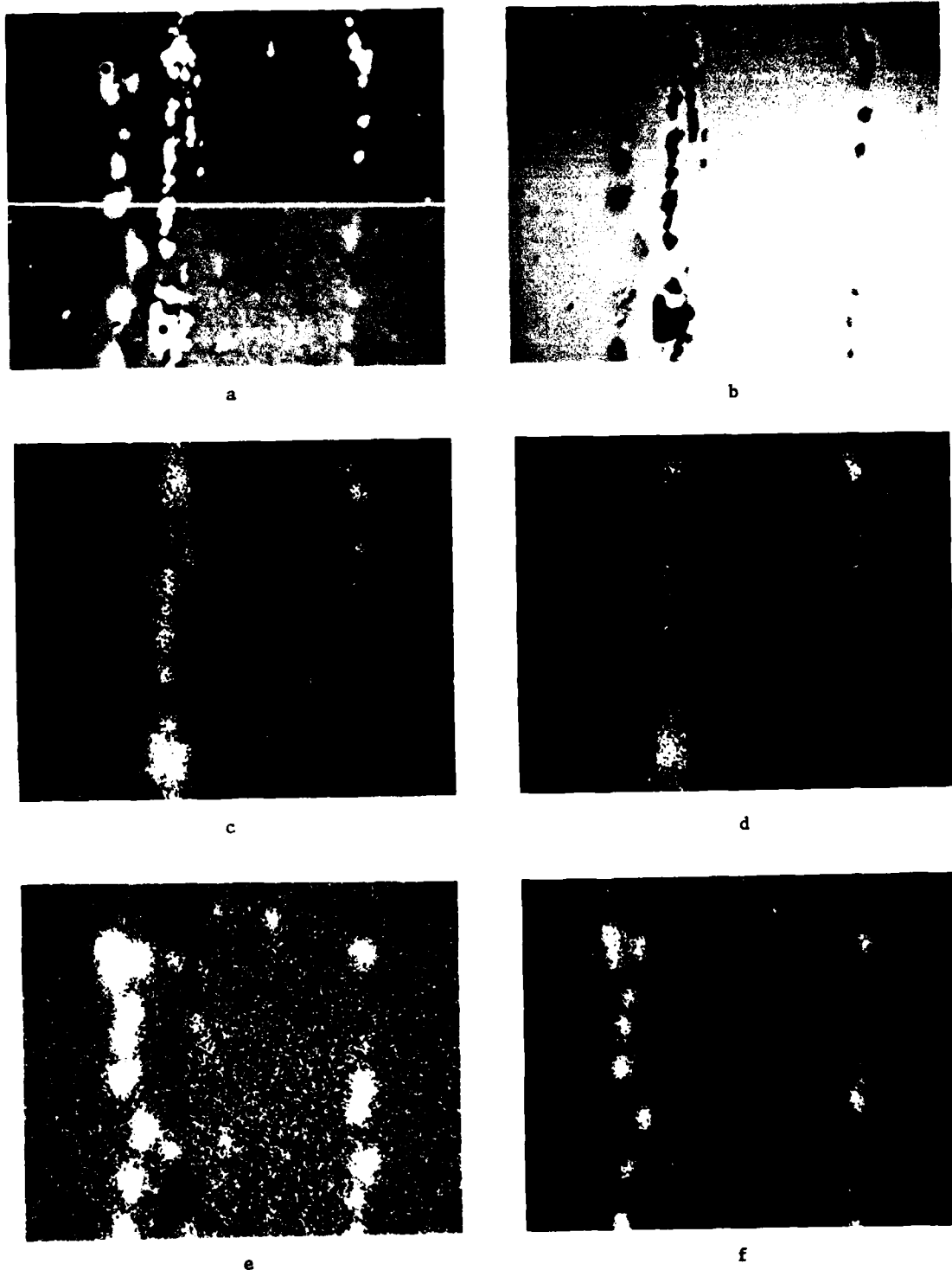


Fig 1a-f (a) Backscattered electron image, (b) specimen current image,  
 (c-f) X-ray images for Cu, Fe, Mg and Si respectively 1000x

Fig 2

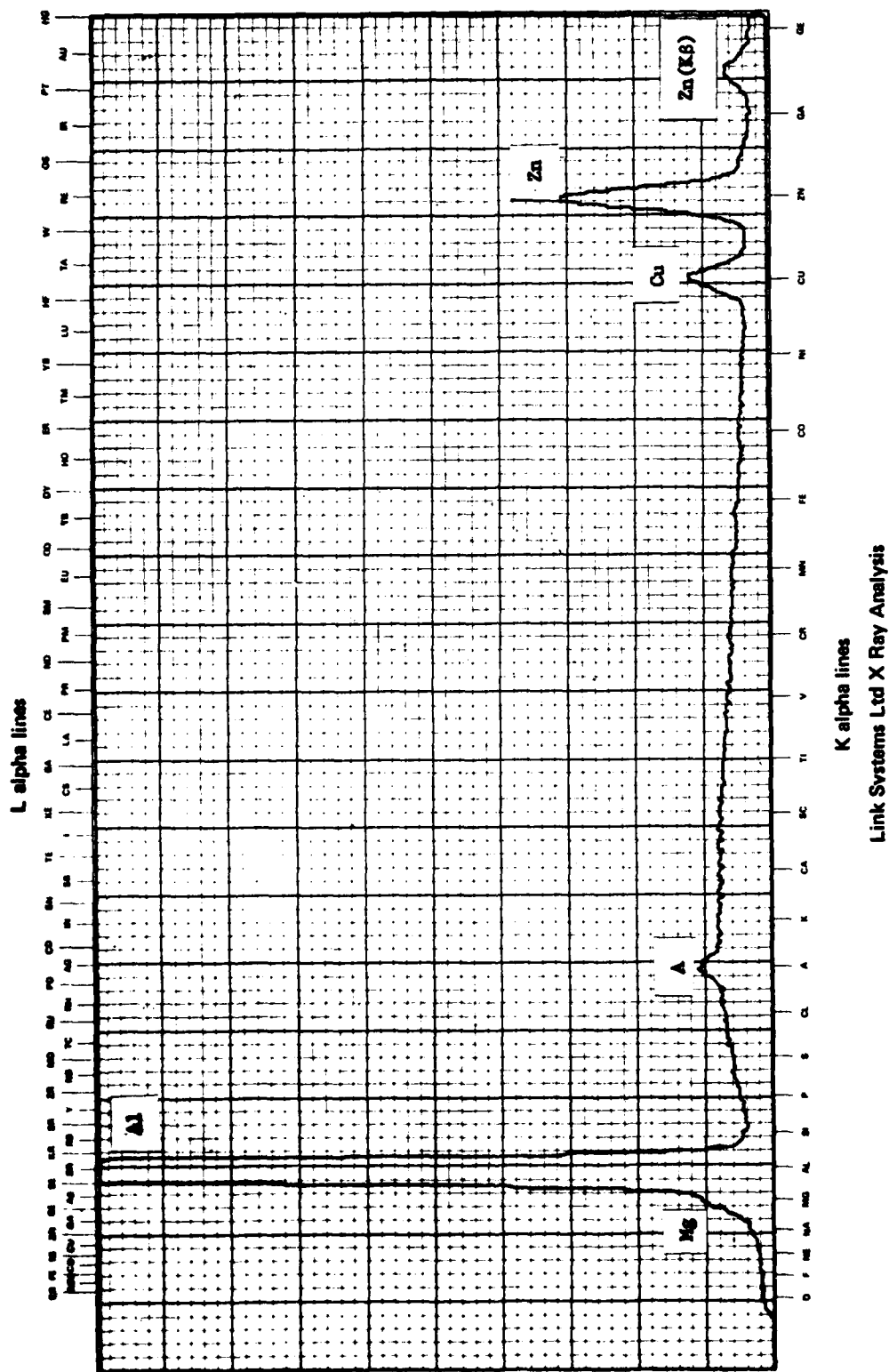
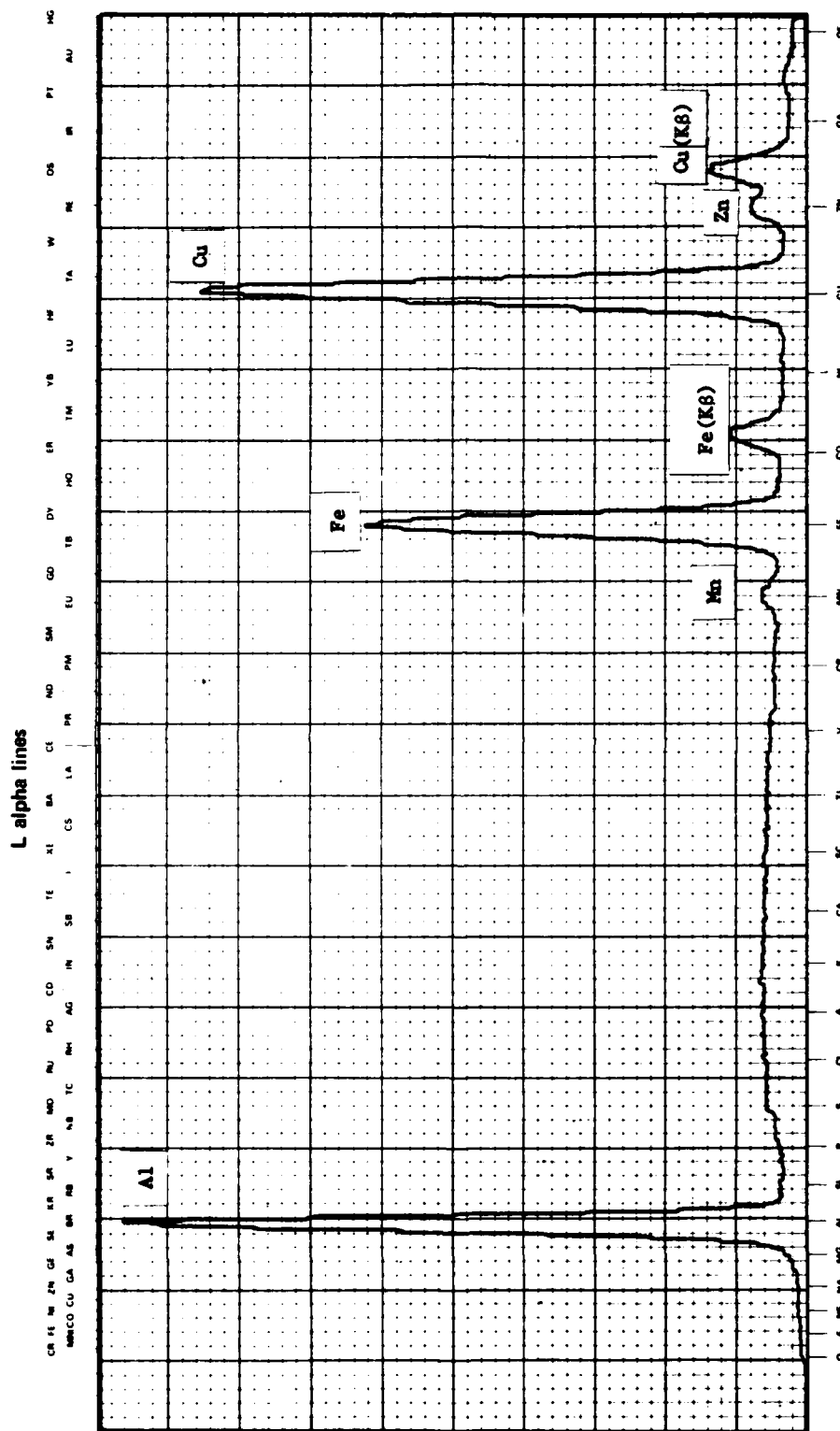


Fig 2 X-ray spectrum for spot A in Fig 1a, (matrix)



**K alpha lines**  
Link Systems Ltd X Ray Analysis

**Fig 3** X-ray spectrum for spot B in Fig 1a, (inclusion rich in Cu and Fe)

Fig 4

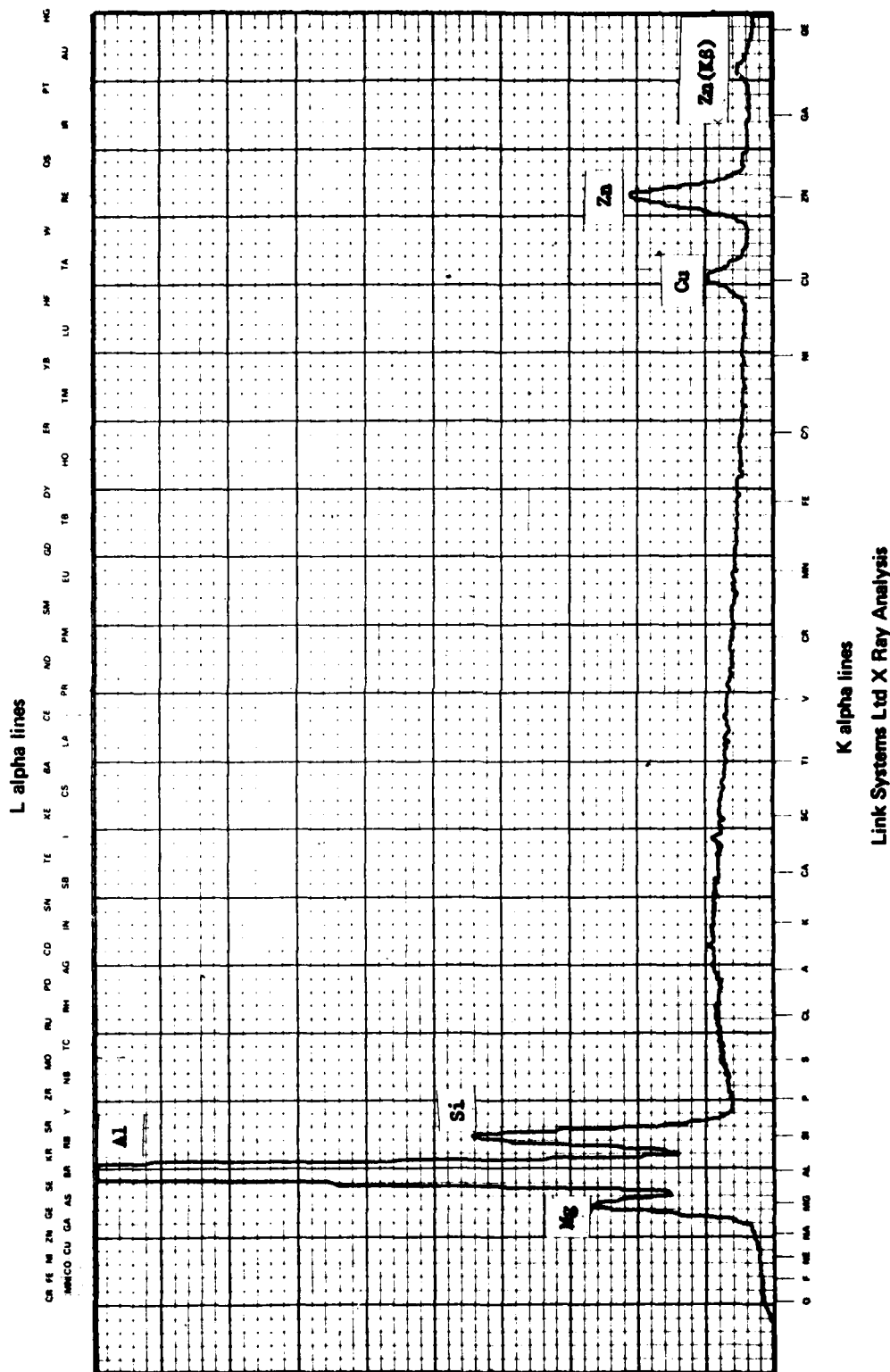


Fig 4 X-ray spectrum for spot C in Fig 1a, (inclusion rich in Mg and Si)

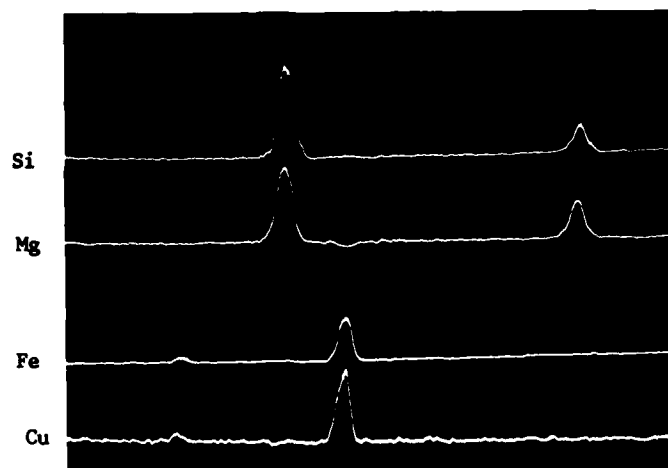


Fig 5 X-ray line scans for the elements indicated, corresponding to line X-X in Fig 1a

STS;.003,.024,0,0  
 #SSE;MG  
 #GO

STANDARD  
 5.00\*10<sup>-8</sup>

DATE 3 6 80 TIME 12 25 50

	X26.847	Y20.385	Z17
MG	B22.232	451.5	
	X26.850	Y20.385	Z17
MG	B22.232	578.2	
	X26.853	Y20.385	Z17
MG	B22.232	664.6	
	X26.856	Y20.385	Z17
MG	B22.232	1121.3	
	X26.859	Y20.385	Z17
MG	B22.232	4522.6	
	X26.862	Y20.385	Z17
MG	B22.232	4134.4	
	X26.865	Y20.385	Z17
MG	B22.232	1181.4	
	X26.868	Y20.385	Z17
MG	B22.232	669.4	
	X26.871	Y20.385	Z17
MG	B22.232	599.0	
			4.99*10 <sup>-8</sup>

DATE 3 6 80 TIME 12 29 7

#

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Fig 6 Print-out of results for step scanning of specimen, with spectrometers set up for Mg only. See text for interpretation

Fig 7

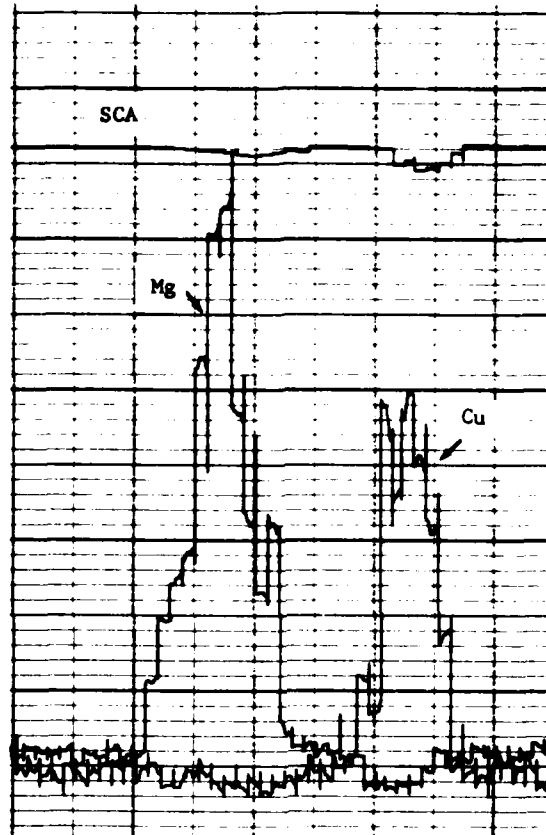


Fig 7 Step scanning of specimen using chart recorder to monitor count rates for Cu and Mg. Peaks correspond to inclusions, either Cu-rich or Mg-rich. Specimen current (SCA) is also monitored



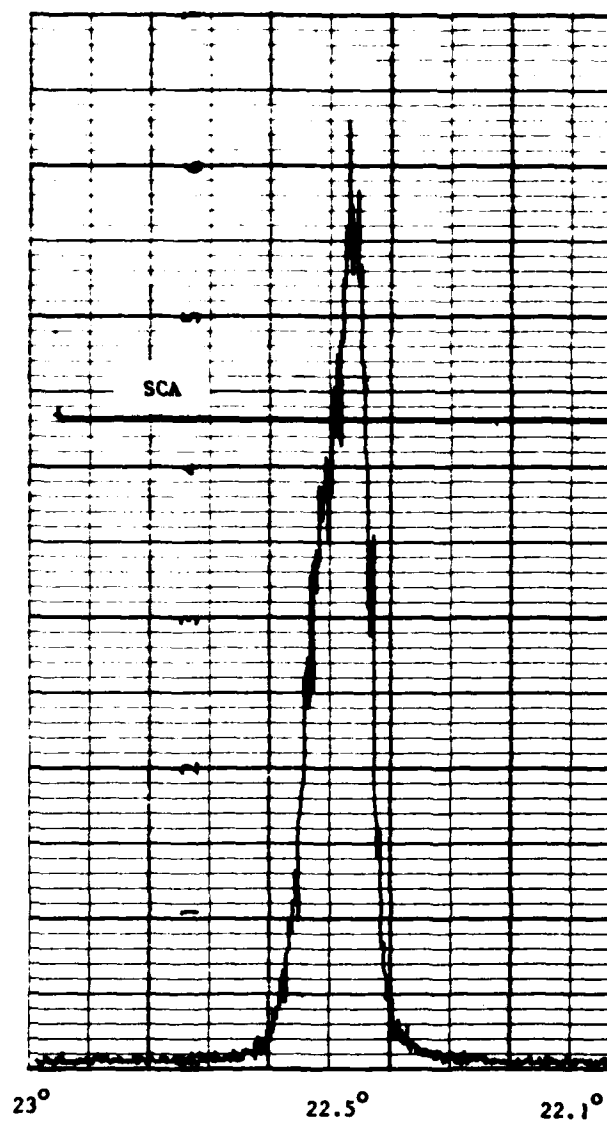


Fig 8 Spectral scanning; Cu peak

Fig 9

GAP:25  
 #MPS:AL,ZN,MG,CU,ZR,FE,SI  
 #AVS:3  
 #BLT:2  
 #GO

ENTER GENERAL ANALYSIS MODE  
 MEASURE PURE STANDARDS  
 TAKE 3 READINGS AND AVERAGE  
 BLANKET ANALYSIS TIME (2 seconds)  
 INITIATE PROGRAM

STANDARD  
 5.00\*10<sup>-8</sup>

DATE 1 6 80 TIME 14 39 50  
 25 KU

	angle	gross c/s	background c/s		net c/s	2σ	ZAF factor
			+	-			
FE	A28.737	12017.7		15.5	12002.2	155.4	0.447455
FE	A28.737	11918.6		16.1	11902.5	154.4	0.447455
FE	A28.737	11900.5		13.1	11887.4	154.4	0.447455
Cu	A22.482	9317.0	17.1		9299.9	136.9	0.467782
Cu	A22.482	9247.1	23.3		9223.8	135.9	0.467782
Cu	A22.482	9218.1	20.3		9197.8	135.9	0.467782
ZN	A20.866	7745.1		22.3	7722.8	124.4	0.468817
ZN	A20.866	7869.9		33.1	7836.8	125.5	0.468817
ZN	A20.866	7837.6		31.1	7806.5	125.5	0.468817
ZR	A43.957	13817.6		68.3	13749.3	166.4	0.358136
ZR	A43.957	13641.8		65.8	13576.0	165.4	0.358136
ZR	A43.957	13631.4		64.2	13567.2	165.4	0.358136
MG	B22.232	40855.2		6.1	40849.1	285.9	0.311846
MG	B22.232	40930.1		7.6	40922.5	286.5	0.311846
MG	B22.232	40954.7		5.6	40949.1	286.5	0.311846
AL	B18.571	58959.0	44.9		58914.1	343.5	0.333987
AL	B18.571	59182.8	45.5		59137.3	344.4	0.333987
AL	B18.571	59096.1	42.9		59053.2	343.9	0.333987
SI	B15.794	58388.2	94.6		58293.6	341.9	0.336367
SI	B15.794	58158.6	92.7		58065.9	341.4	0.336367
SI	B15.794	57432.9	105.5		57327.4	338.9	0.336367

4.88\*10<sup>-8</sup>

DATE 1 6 80 TIME 14 54 18

\*

Fig 9 Results print-out of measurements on pure standards.  
 The columns have been headed to assist interpretation

GAP:25				MEASURE UNKNOWN			
#UNK				ANALYSE THESE ELEMENTS			
#STD:AL,ZN,MG,CU,ZR,FE,SI				PERFORM ZAF CORRECTION			
#ZAF							
#GO							
STANDARD							
5.00*10^-8							
DATE 1 6 80 TIME 14 57 8							
25 KV							
				UR			
X24.611 Y23.997 Z17							
FE	A28.737	7.2		6.9	0.3	1.6	0.00 0.01
MG	B22.232	580.0		32.3	547.7	15.3	1.33 0.03
CU	A22.482	141.5	9.4		132.1	7.6	1.42 0.08
AL	B18.571	42904.0	31.8		42872.2	131.1	72.62 0.22
ZN	A20.866	451.0		11.0	440.0	13.4	5.64 0.17
SI	B15.794	35.4	38.9		0.0	3.8	0.00 0.01
ZR	A43.957	22.6		7.0	15.6	3.1	0.11 0.02
***							
TOT				81.12 0.53			
UR CR							
ZAF	COR	4 ITER					
MG	1.33	1.71	2.83				
AL	72.62	89.68	169.45				
SI	0.00	0.00	0.00				
FE	0.00	0.00	0.00				
CU	1.42	1.68	2.10				
ZN	5.64	6.66	8.29				
ZR	0.11	0.22	0.30				
***							
TOT				81.12 99.95 182.97			
5.01*10^-8							
DATE 1 6 80 TIME 15 1 14							

Fig 10 Results of analysis on unknown. Uncorrected results are indicated by UR, and corrected results by CR

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The basic principles of electron microprobe analysis are outlined, and the essential features of the Microscan 9 instrument described. Applications of the instrument are illustrated by means of practical examples.